A

Thesis

On

ADSORPTIVE REMOVAL OF DYES FROM AQUEOUS SOLUTION USING Cu-BTC AND COMMERCIAL ACTIVATED CARBON

Submitted by

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In partial fulfillment of the requirements for the degree in

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Under the guidance of

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MAY, 2012

National Institute of Technology Rourkela

CERTIFICATE

*This is to certify that the project report entitled, "**Adsorptive removal of dyes from aqueous solution using Cu-BTC and Commercial Activated Carbon**", submitted by **Deepak Garg** (108CH010) in partial fulfillments for the requirements for an award of Bachelor of Technology Degree in Chemical Engineering at National Institute of Technology Rourkela is prepared by him under my supervision and guidance and this work is not been submitted elsewhere for a degree.*

_____

Date: 7th May, 2012

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Deepak Garg

ABSTRACT

This thesis is dedicated to the liquid phase adsorption of dyes, namely Rhodamine B and Erioglaucine, where they represent the class of a basic and an acid dye respectively. The adsorbents used are Metal Organic Framework (Cu-BTC) and Activated Carbon. The characterization was done for each of the adsorbent. On the one hand, the experimental data did not envisage Cu-BTC as an effective adsorbent for liquid phase adsorption while on the other hand, Activated Carbon showed some encouraging results on the batch experiments conducted on various parameters like effects of adsorbent dose, initial pH and contact time.

Keywords: Rhodamne B , Erioglaucine, Metal Organic Framework, Cu-BTC, Activated Carbon

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NOMENCLATURES

- SEM = Scanning Electron Microscope
- XRD = X-Ray Diffraction
- BET = Brunauer-Emmett-Teller
- TGA = Thermo Gravimetric Analysis
- MOF = Metal Organic Framework

CHAPTER 1

INTRODUCTION

1.1 Prelude

So far, our earth is the only planet in the whole universe, accredited to have life. One of the prime reasons, which support life in our mother-planet, is water. But, anthropogenic activities have caused a great harm to the quality of our lifeline, i.e. water. Because of fast depletion of the freshwater resources, there seems to be a crisis of the same. Water pollution is a global concern and, it is the high time that we realize the gravity of the situation. Removing pollutants from water is the crying need of the hour and developing a cost effective and environmentally safe method to achieve the same is a challenging task for chemical engineers. After all, it is the future of mankind, which is at stake.

A dye is a colored substance that has an affinity to the substrate to which it is being applied. Dyes appear to be colored because they absorb some wavelengths of light more than others. Humans are estimated to use dyes for thousands of years and the earliest use of the colorant is believed to be by Neanderthal man about 1,80,000 years ago [1, 2]. The year 1856 witnessed a historic discovery of first synthetic dye, Mauvine, by Perkin [3, 4]. In due course of time, these synthetic dyes gained huge popularity and began to be synthesized on a large scale. In fact, it has reached to a level of annually, over 7.0×10^5 and nearly 1000 different types of dyes are produced worldwide [5].

1.2 Background of Present Research

Now-a-days, a large amount of waste water having color is generated by many industries like textile, leather, paper, printing, plastic and so on [6]. The presence of dye materials greatly influence the quality of water and the removal of this kind of pollutant is of prime importance. Owing to their complicated chemical structures, dyes are difficult to treat with municipal waste

treatment operations [5]. Even a small quantity of dye does cause high visibility and undesirability. Moreover, the color produced by dyes in water makes it aesthetically unpleasant [6]. They can have acute or chronic effects on exposed organisms, which depend on the concentration of the dye and the exposed time [5]. In addition to that, many dyes are considered to be toxic and even carcinogenic [6-8].

Few decades earlier the dye selection, applications and uses were not given much importance. With the growing health concerns, it was in the 80s that people started paying much attention to the dye wastes [2]. An indication to the magnitude of this problem can be inferred from the fact that two percent of dyes produced are directly discharged into aqueous effluents [9, 10]. With the increased stringent laws on industrial discharge, it has become very important to treat this wastewater. Because of their detriment and large scale distribution in the ecological environment, their separation and determination has become one of the important studies of environmental analysis. Of prime importance is the need for clear information on the safety related properties of the colorants and the measure to be taken for lowering exposure. If all these elements are seriously considered, then the technical use of colorants and the handling involved might be possible without much health danger.

1.3 Research Objectives

Several physical, chemical and biological de-colorization methods such as coagulation/flocculation treatment, biodegradation processes, oxidation methods, membrane filtration and adsorption have been reported to be investigated for the removal of dyes from industrial effluents [11-14]. Among the studied methods, removal of dyes from adsorption is found to be the most competitive one because it does not need a high operating temperature and

several coloring materials can be removed simultaneously [6]. The versatility of adsorption is due to its high efficiency, economic feasibility and simplicity of design [8]. As there are various parameters to effect adsorption process such as, charge density and structural stability of the adsorbent so, in the thrust of a comprehensive study, we have selected one basic dye (Rhodamine B) and one acidic dye (Erioglaucine) for this present study.

Several adsorbents have been used for this purpose such as some natural adsorbents (e.g., clay, cellulosic materials, chitin and chitosan) [15-20]. Agricultural wastes such as lemon [21] and banana and orange peel [22] have also been used. Functionalized adsorbents such as hyper-crosslinked polymers [23] and diaminoethane sporollenin [24] have also been studied for this purpose.

One of the conventional and most studied adsorbent is Activated Carbon (AC). The reasons for this popularity are its high adsorption capacity, high surface area and microporous structure [5]. In fact, Activated Carbon adsorption has been listed by the US Environmental Protection Agency as one of the best available control technologies [25].

Metal-organic frameworks (MOFs) are crystalline materials which are very popular for various applications [26-33]. The special interest in MOFs is due to the easy tunability of its pore size and shape from a microporous to a mesoporous scale [26-28]. MOFs have special interest in the adsorption, separation and storage of gases and vapors [29-32]. The MOF selected for our study is Cu-BTC. However, there has not been much report on the use of MOFs in the removal of dye materials. But MOFs have certainly, attracted increasing interest due to their rich structural chemistry and tunable physical properties.

Thus our objective is to study the effects of Cu-BTC (a novel adsorbent) and activated carbon (conventional adsorbent) in removing the dyes *viz*. Rhodamine B and Erioglaucine from aqueous medium.

CHAPTER 2

LITERATURE REVIEW

2.1 Adsorption Principles

Adsorption is a process that occurs when a gas or liquid solute accumulates on the surface of a solid or a liquid, forming a molecular or atomic film. In other words, adsorption is the adhesion of atoms, ions, biomolecules or molecules of gas, liquid, or dissolved solids to a surface and this process creates a film of the adsorbate (the molecules or atoms being accumulated) on the surface of the adsorbent. It is a surface phenomenon and a consequence of surface energy. The atoms on the surface of the adsorbent are not wholly surrounded by the other atoms and thus, can attract adsorbates. The exact nature of the bonding depends on the details of the species involved, but the adsorption process is generally classified as follows:

(1) Physisorption: It is a type of adsorption in which the adsorbate adheres to the surface through Van der Walls (weak intermolecular) interactions.
(2) Chemisorption: It is a type of adsorption whereby a molecule adheres to a surface through the formation of a chemical bond.

Adsorption takes place primarily on the walls of the pores or at specific sites inside the particle. As the pores are generally small, the internal surface area is greater than the external area. Separation occurs because differences in molecular weight, shape or polarity cause some molecules to be held more strongly on the surface than others. In many cases, the adsorbate is held strongly enough to allow complete removal of that component from the fluid [34].

2.2 Basics on Dyes

As discussed earlier, dyes are an important class of pollutants and can even be recognized by human eyes. A dye molecule consists of two key components: the ***chromophores***, responsible

for producing the color, and the ***auxochromes***, which in addition to support the chromophore, also render the molecule soluble in water and give enhanced affinity toward the fibers. Dyes have high structural diversity and can be classified in many ways [2]. Some properties of dyes are based on their usage and can be broadly classified as [1-3]:

2.2.1 Acid dyes

It is a sodium salt of a sulfonic, carboxylic or phenol organic acid. It is soluble in water and possesses affinity for amphoteric fibres. It is used for nylon, wool, paper, leather, food, cosmetics etc.

2.2.2 Basic dyes

They yield colored cations in solution and this is the reason for calling them cationic dyes. This type of dye finds uses in paper, modified nylons and polyesters, medicine etc.

2.2.3 Direct dyes

These are water soluble anionic dyes. These are used for dyeing of cotton and rayon, paper, leather etc.

2.2.4 Disperse dyes

These are substantially insoluble nonionic dyes. These are used mainly on polyester and also applied on nylon, cellulose, acrylic fibers etc.

2.2.5 Sulfur dyes

These types of dyes have intermediate structures. They form a relatively small group of dyes, but the low cost and good wash fastness properties make it very important from the economic point of view. Its main uses are for cotton and rayon.

2.2.6 Reactive dyes

They have a chromophore attached to a substituent that is capable of directly reacting with the fiber substrate. The prime reason to make them classified among the most permanent of dyes is the covalent bond that attaches reactive dyes to natural fibers. They find their uses for cotton, wool and nylon.

2.2.7 Solvent dyes

These type of dyes are generally non-polar or little polar and thus, are water insoluble. They are used for plastics, gasoline, lubricants, oils etc.

2.2.8 Vat dyes

This type of dye is water insoluble and incapable of dyeing fibers directly. But, reduction in alkaline liquor produce the water soluble alkali metal salt of the dye, which, in this leuco form, has an affinity for the textile fiber. These are used mainly for cotton, wool and nylon.

2.3 Reviews on Some Recent Works on Dyes

Several studies have been conducted on the adsorption of different dyes from various adsorbents.

In 2011, dye removal from colored textile wastewater using chitosan in binary system was studied [35]. Here, Direct Red 23 and Acid Green 25 were used as anionic dyes. The adsorption

kinetics of dyes on chitosan followed the pseudo second order at different pH values. The experimental data were correlated reasonably well by Tempkin adsorption isotherm. It was concluded that the chitosan is an eco- friendly adsorbent for dye removal from low concentration of acidic colored textile wastewater.

In 2010, chemically modified sugarcane bagasse as a potentially low-cost biosorbent for the removal of methyl red was studied [36]. The kinetics of methyl red adsorption followed the pseudo first order kinetic expression and Langmuir isotherms model fit well. From the study, it was inferred that sugarcane bagasse has a good potential to be used for small scale industries, which produces dyes as their effluent, after it was being pretreated with phosphoric acid.

In 2009, active manganese oxide was studied for the treatment of wastewater containing congo red [37]. The equilibrium data was very well represented by the Langmuir and Freundlich isotherms as well as well as a pseudo second order kinetic model.

In 2010, coconut and coffee husks were identified as potential biosorbents for removal for hazardous dye, Quinoline yellow [38]. The equilibrium data fitted well to the pseudo first order model and conform to the Langmuir and Freundlich isotherms. The results also showed that the reaction was exothermic.

In 2010, the removal of reactive red 23, reactive blue 171, acid black 1 and acid blue 193 from aqueous solution using fly ash was studied [39]. The results showed that adsorption was pH dependent, adsorption increased with the initial dye concentration; the reaction was spontaneous and exothermic in nature.

In 2010, the porous magnetic microspheres prepared with sulfonated macroporous polydivinylbenzene as a template and their ability to remove cationic dyes was studied [40]. The

results show that methyl violet and basic fuchsin can be successfully removed from the adsorbent used and even the adsorbent is easily regenerated.

2.4 Basic Dye (RHODAMINE B)

Basic dyes have amino groups, or alkylamino groups, as their auxochromes, and consequently have an overall positive charge. In other words, the colored part of the molecule is the cation. Although the molecule charge is often shown on a specific atom in structural formulae, it is the whole molecule that is charged. They are brilliant and most fluorescent among all synthetic dyes but have poor light and wash fastness.

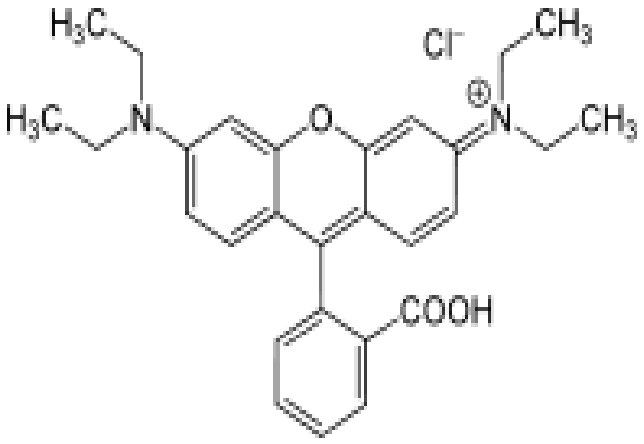

Figure 2.1: Structure of Rhodamine B [43]

IUPAC Name: 9-(2-carboxyphenyl)-6-diethylamino-3 anthenylidene) diethylammoniumchloride

Molecular formula = $C_{28}H_{31}ClN_2O_3$

Molar mass = 479.02 gram $mole^{-1}$

Appearance = red to violet powder

Melting point = 210-211^{o}C (with decomposition)

Rhodamine B is used as dye, especially for paper. It is also used as a reagent for antimony, bismuth, cobalt, niobium, gold, manganese, mercury, molybdenum, tantalum, thallium and tungsten. Besides these, it is also provisionally listed for use in drugs and cosmetics. On the other hand, this dye is also very toxic. Chronic exposure may cause nausea and vomiting, higher exposure causes unconsciousness.

2.5 Acid Dye (ERIOGLAUCINE)

Acid dyes are dyes, in chemical regard, a sodium (less often-ammonium) salt of a sulfonic, carboxylic or phenol organic acid. Acid dye is soluble in water. When dyeing, ionic bonding with fiber cationic sites accounts for fixation of colored anions in the dyed material. The chemistry of acid dyes is quite complex. Dyes are normally very large aromatic molecules consisting of many linked rings. Acid dyes usually have a sulfo or carboxy group on the molecule making them soluble in water. Acid dyes are thought to fix to fibers by Hydrogen bonding, Vander Walls forces and ionic bonding. They are normally sold as the sodium salt; therefore, they are in solution anionic.

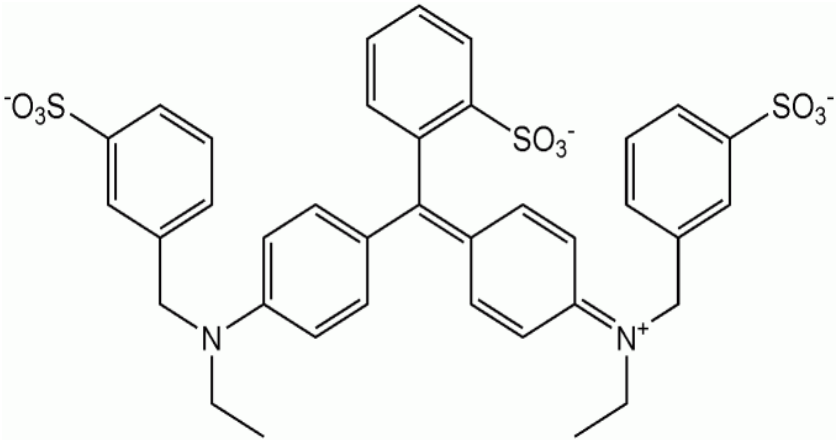

Figure 2.2: Structure of Erioglaucine [43]

IUPAC Name: ethyl-(4-((4-9ethyl-(3-sulfophenyl) methyl) amino) phenyl)-(2-sulfophenyl) methylidene)-1-cyclohexa-2, 5-dienylidene)-((3-slfophenyl) methyl) azanium

Molecular formula: $C_{17}H_{34}N_2Na_2O_9S_3$

Molar mass: 792.86 gram $mole^{-1}$

Appearance: red (dark)

This dye is popularly known as brilliant blue FCF. It is a synthetic dye produced using aromatic hydrocarbons from petroleum. As a blue color, it is often used in ice cream, canned processed peas, packet soups, bottled food colorings, dairy products, sweets and drinks. It is harmful, if contacted with skin or eye. This dye is also very toxic to kidneys. Repeated or prolonged exposure to the substance can damage the target organs.

In 2009, usage of agro-industrial waste for the removal of basic dyes was studied [41]. The experimental data showed that various adsorbents used, such as sawdust and sugarcane fibers were effective in the removal of Rhodamine B and Crystal Violet.

In 2009, the removal of Rhodamine B in aqueous solution was studied with a carbon adsorbent prepared from acid activated banana bark carbon [42]. The study was done for various parameters like pH, temperature etc. The experimental data were correlated reasonably well with the Langmuir and Freundlich isotherms.

In 2007, application of MCM-41 for dyes removal of many dyes, including Rhodamine B and Erioglaucine, from wastewater was studied [43]. The adsorption capacity of MCM-41 was found to be greater for Rhodamine B than that of Erioglaucine. The equilibrium data of Rhodamine B (basic dye) correlated reasonably well for Langmuir adsorption isotherm. The adsorption kinetics was found to follow the pseudo second order model and the external diffusion was specified as the controlling process.

In 2006, application of MCM-22 was studied for the removal of three basic dyes, including Rhodamine B was studied [44]. The experimental data indicated that the adsorption followed a pseudo second order kinetic model. The adsorption was found to be a two step diffusion process with film diffusion dominating the process. The adsorption isotherms were correlated well by both Langmuir and Freundlich models.

In 2005, a comparative study of removal of some dyes, including Rhodamine B, from aqueous solution was investigated for fly ash treated by methods like conventional chemical, sonochemical and microwave [45]. It was found that adsorption capacity of HCl treated fly ash varies with the preparation conditions. The results showed microwave treatment as a fast and efficient method for producing the sample with the highest adsorption capacity. The experimental data fitted well with the Freundlich and Redlich-Peterson models.

2.6 Metal Organic Frameworks

2.6.1 Definition

Metal organic frameworks or MOFs represent a class of novel adsorbents that have attracted the researches all round the world due to its great diversity in structures resulting from co-ordination bonds between inorganic metal atoms as nodes and organic ligands as linkers. Porosity, crystallinity and product purity are some of the key attributes of MOFs [46]. They consists of a metal ion or clusters coordinated to often rigid organic molecules to form one, two, three dimensional structures that can be porous. MOFs are relatively new microporous structures. The particular interest in MOF is due to due to the easy tunability of their pore size and shape from a micro to a meso scale by changing the connectivity of the inorganic part and the nature of the organic linkers. They can often be considered as expanded versions of typical inorganic structures where organic components act as linkers to connect inorganic clusters, chains or layers. MOFs are known to have many applications [26-33].

Before being explored effectively at industrial level, there are some concerns which need proper attention. It has been observed that surface area and pore volume of the same MOF synthesized by different researches at different parts of the world are different. The same observations have also been found on the different batches of MOF prepared on a single location. The reason behind this anomaly alludes at different synthesis conditions and post- treatment thereafter [46].

2.6.2 Cu-BTC (or, HKUST-1 or, MOF-199)

Cu-BTC [$Cu_3(BTC)_2$, BTC = Benxene 1,3,5 tricarboxylate] also known as HKUST-1 is one of the widely studied MOF. It was reported for the first time in 1999 [47]. Thereafter, there was a

growing interest in the study of this adsorbent and various methods were developed to improve the synthesis and characterization of this highly promising adsorbent [48-50].

There are not much report of the use of MOFs in the removal of dye materials. For the first time in 2010, the study of adsorptive removal of dye (methyl orange) from aqueous solution was studied with MOF (Cr-BDC) [51]. Here, two highly porous MOF materials, MIL-53 and MIL-101 were studied. MIL -101 showed greater values of adsorption capacity and kinetic constant, showing the importance of porosity.

As with the case with other MOFs, Cu-BTC also has been majorly studied for gaseous adsorption. However, to the best of our knowledge, no study has been done on the use of Cu-BTC for dye removal from aqueous solution.

2.6.3 Activated Carbon

Activated carbon is the conventional and most studied adsorbent. The ability of charcoal to remove odor and taste was observed centuries ago. According to a Sanskrit manuscript from circa 200 BC," it is good to keep water in copper vessels, to expose it in sunlight and to filter it through charcoal." [52, 53]. However, the credit of developing commercial activated carbon goes to Raphael von Ostrezko [54].

Activated carbon is porous material which is commercially used for the removal of liquids and gases pollutants owing to its large surface area. It is a carbonaceous adsorbent and has known to have highly amorphous structure [55]. It has been observed that adsorption on activated carbon is not usually selective as it occurs through weak Van der Walls forces [2].

In 2009, the study of preparation of activated carbon from digested sludge of the tannery industry was done for the removal of a reactive dye [56]. The experimental data correlated well with the Langmuir, Freundlich and Temkin adsorption isotherms.

In 2011, the study was done on the ability of activated carbon in the removal of two anionic dyes (Direct Blue 78 and Direct Red 31) from colored wastewater in single and binary systems [57]. The effects of adsorbent dosage and initial dye concentration were studied at 25^{o}C. The kinetics was found to conform to pseudo second order kinetic model. The equilibrium data fitted well with Langmuir adsorption isotherm. Results indicated that Activated Carbon is an effective adsorbent in this case.

In 2010, competitive adsorption of dyes (congo red, methylene blue, malachite green) on activation carbon was studied [5]. It was found that the percent removal of color increased with the increase in the amount of adsorbent dosage and also with the increase in contact time. It was also observes that the adsorption varies with changing the value of pH of dye solution.

In 2001, the study of methylene blue adsorption on commercial activated carbon and indigenously prepared activation carbon from bamboo dust, coconut shell, groundnut shell, rice husk and straw was done [58]. The effects of various experimental parameters were investigated. The experimental data fitted well with the Langmuir and Freundlich adsorption isotherms. The results also indicated that the indigenous activated carbon can be employed as low cost alternative to the commercial activated carbon.

In 2002, the study was done the removal of a direct dye by adsorption onto coal based adsorbents viz. charfines, lignite coal, bituminous coal and comparing results with activated carbon [59].

The investigation indicated that the coal based sorbents facilitated chemisorption in the process of dye sorption while, activated carbon resulted in physisorption interactions.

CHAPTER 3

MATERIALS AND METHODS

3.1 MATERIALS

3.1.1 GLASSWARES AND APPARATUS USED

All glassware (conical flasks, measuring cylinders, beakers, pipettes etc.) were manufactured by Borosil / Rankem. All the instruments and apparatus used in the experiment are listed below:

Table 1: list of all instruments used

INSTRUMENT	MANUFACTURER / TYPE	FUNCTION
Electronic weight balance	Sartorius	To measure weight
pH meter	EuTech Instruments	To measure Ph
Oven	Shivaki	To dry the samples / to maintain the temperature
Shaker	Environmental orbital shaker incubator	To shake the samples in dye solutions
Spectrophotometer (UV/ Vis)	Jasco (V 530)	Absorbance
Thermo Gravimetric Analyzer (TGA)	Shimadzu (DTG 60 H)	Thermal analysis
Scanning Electron Microscope (SEM)	JEOL JSM-6480 LV	Morphology

X-Ray Diffractometer (XRD)	Philips Analytical, PW-3040	X-ray diffraction
Brunauer-Emmett Teller (BET)	Quantachrome (Autosorb)	Surface Area Analysis

3.1.2 SYNTHESIS OF Cu-BTC

The synthesis of Cu-BTC was done on the basis of the earlier reported method [47].

0.33 grams of benzene 1, 3, 5 tri-carboxylic acid (BTC) was dissolved in 10 ml solution of ethanol and N, N Dimethyl Formamide (DMF), each with an equal proportion of 5 ml. After this, copper (II) nitrate trihydrate ($Cu(NO_3)_2.3H_2O$) weighing 0.692 grams was dissolved in 5 ml water. Both the solutions were mixed and stirred for 10 minutes. Then, the final solution was put in the autoclave. After this, the autoclave was put in the oven at 100^oC for 10 hours. After the given time, the autoclave was taken out from the oven and allowed to cool. Then, the filtration was done to separate the crystals. Then, it was dried in the oven for 2 hours at 100^oC. After taking it out from the oven, it was washed with methanol. Then, again, it was put for drying for 2 hours at 100^oC. In the end, it was taken out from the oven and stored in desiccator. The same procedure was repeated and a total of three batches of Cu-BTC were made.

3.1.3 POWDERED ACTIVATED CARBON

The commercial activated was purchased from MERCK. It was used without any improvisation. The adsorbent used was dried at 70^oC for 24 hours before use.

3.1.4 DYES

Rhodamine B (λ_{max} = 555 nm) was purchased from LOBA CHEMIE. It was used without any improvisation or further purification.

Erioglaucine (λ_{max} = 630 nm) was purchased from LOBA CHEMIE. It was used without any improvisation or further purification.

3.2 METHODS

For the experimental work on Cu-BTC, the stock solution of 10^{-4} M was made for both the dyes. Working solution was selected as 10^{-5} M. The calculations are shown in ***appendix 1***.

In case of commercial activated carbon, the values for stock solution and working solution for both the dyes were 1000 mg/l and 20 mg/l respectively. The detail calculations are shown in ***appendix 2*** in tabular form.

Dye concentrations were estimated spectrophotometrically at the wavelength corresponding to maximum absorbance, λ_{max}.

3.2.1 Effect of adsorbent dose

50 ml of the working solution was put in each different conical flask. Then, different adsorbent dose was added in each flask. All the flasks were kept inside the shaker at 100 rpm and 25^{o}C. After 70 minutes, the flasks were withdrawn from the shaker and the dye solutions were separated from adsorbents by using centrifuge at 4000 rpm for 10 minutes (in case of Cu-BTC) and with the help of filtration (in case of commercial activated carbon. The absorbance of all the

solutions was then measured. A graph was plotted with percent removal ($\%Q$) vs. adsorbent dose. D is expressed as,

$$\%Q = \frac{(C_i - C_o)}{C_i} \times 100 \tag{3.1}$$

Where,

$\%Q$ = percentage of dye adsorbed

C_i = initial dye concentration (mg/lit)

C_o = final dye concentration (mg/lit)

3.2.2 Effect of Initial pH

50 ml of the working solution was put in each different conical flask. The optimum adsorbent dose as obtained from the above study was put in each flask. The pH of each flask was adjusted in the range of 2-12 with dilute HCl (1 M) and NaOH (1 M) solution by the use of pH meter. Then, all the flasks were kept inside the shaker at 100 rpm and 25^{o}C for 70 minutes. After that, flasks were withdrawn, solution was filtered and absorbance of the solutions was measured. A graph was plotted with $\%\ Q$ vs. initial pH.

3.2.3 Effect of Contact Time

50 ml of the working solution was put in each different conical flask. The results obtained from above two studies of optimum adsorbent dose and initial pH was used here. All the flasks were put in the shaker at 100 rpm and 25^{o}C for a predetermined time period ranging from 10 minutes to 180 minutes. Then, flasks were withdrawn from the shaker, solution was filtered and absorbance of the solutions was measured. A graph was plotted with $\%\ Q$ vs. contact time.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 CHARACTERIZATION OF ADSORBENTS

Thermal analysis of adsorbents was carried out in detail in a TGA apparatus, SHIMADZU (DTG 60 H). The morphologies of the synthesized Cu-BTC product was characterized using a scanning electron microscope (SEM, JEOL JSM-6480 LV) equipped with an energy dispersive X-ray spectrometer (EDX). The synthesized samples were subjected to X-ray diffraction by a diffractometer (XRD, Philips Analytical, PW-3040) equipped with the graphite monochromatized CuKα radiation (λ = 1.5406 Å) in 2θ angles ranging from 5^o to 75^o with a step size of 0.05 degree and scanning rate 2^o per minute.

4.1.1 Characterization of Cu-BTC (or, HKUST-1)

4.1.1.1 SEM Analysis

The surface morphology studies of synthesized Cu-BTC showed octahedral shaped crystals as shown in figure which is similar reports as presented in many literatures.

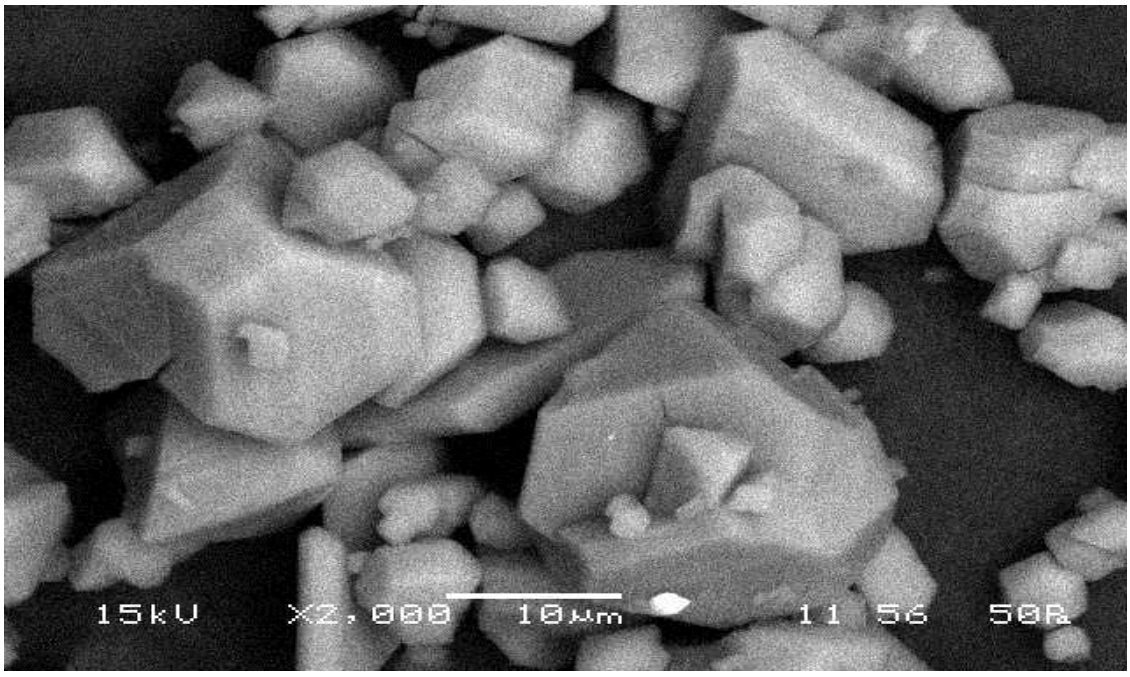

Figure 4.1: SEM Imaging of as-synthesized Cu-BTC

4.1.1.2 Powder XRD Analysis

The powder XRD pattern as shown in figure 4.2, matches well with the literature reports confirming the product. The sharp peaks are confirmation about the crystallinity of Cu-BTC. The product synthesized is also very pure since no additional peaks for any foreign impurity is seen in the pattern.

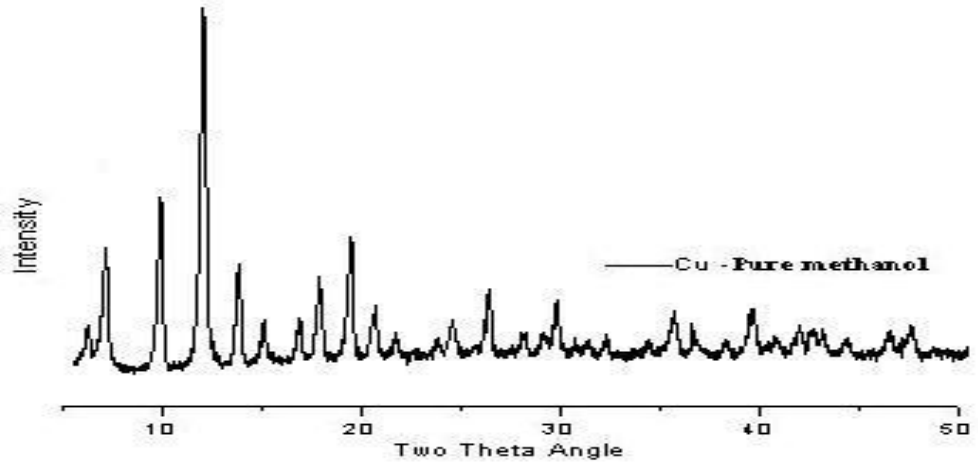

Figure 4.2: Powder XRD Analysis of Cu-BTC Sample

4.1.1.3 BET Surface Area Analysis

The BET surface area performed showed a surface area of 785 m^2/gm, which is comparatively a reasonable value for the synthesized MOF. It should be worth mentioning that more the surface area, more efficient may be the adsorption of dye from aqueous solution.

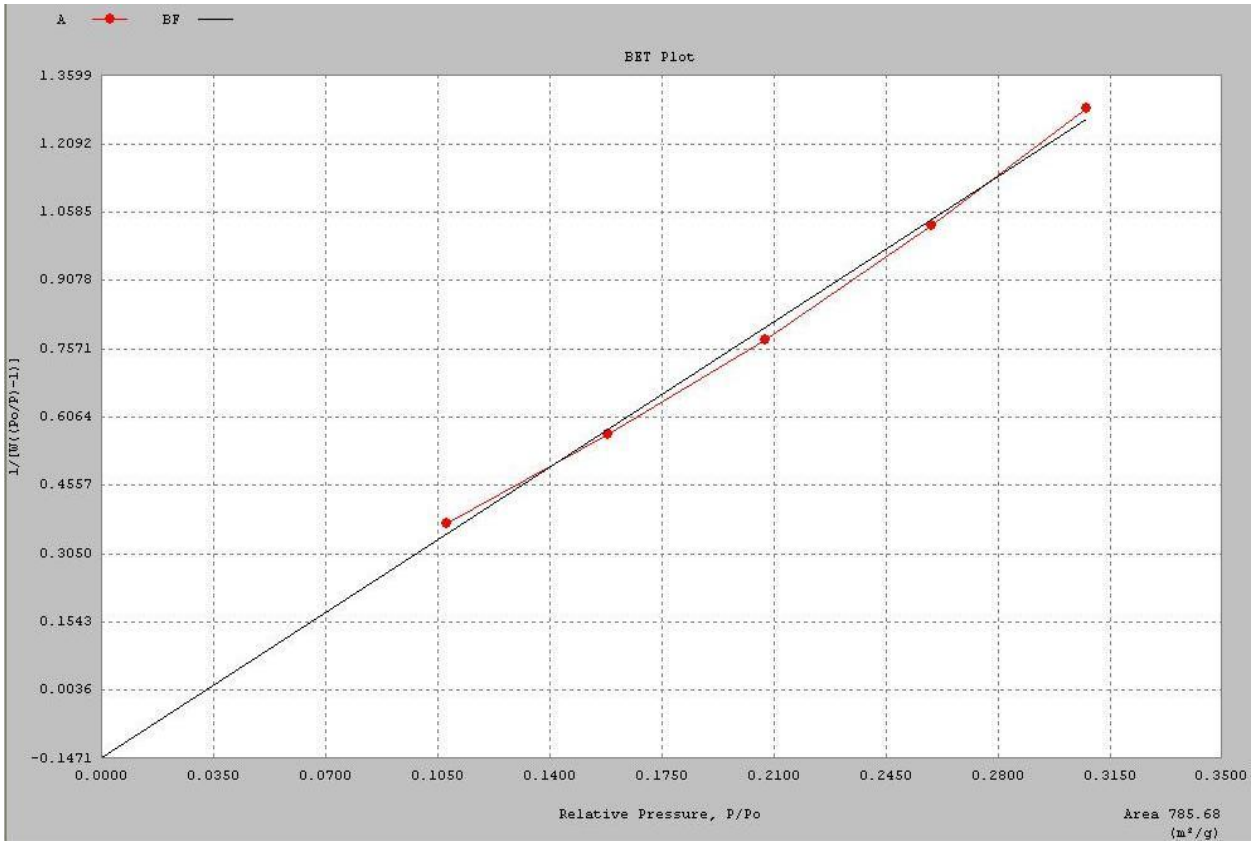

Figure 4.3: BET Surface Area Analysis of Cu-BTC Sample

4.1.1.4 TGA Analysis

The TGA profile shows typical weight loss pattern for the Cu-BTC MOF and complete degradation of Cu BTC starts around 275^{o}C and by 325^{o}C the degradation is complete. In the range between 25-125^{o}C the weight loss is purely due to removal of moisture and trapped methanol and between 125^{o}C to 275^{o}C where the weight remains fairly constant, is stable zone. Thus, for any experimentation using Cu-BTC, the system temperature should be regimentally maintained to be between 125-275^{o}C. Figure 4.4 shows the TGA profile.

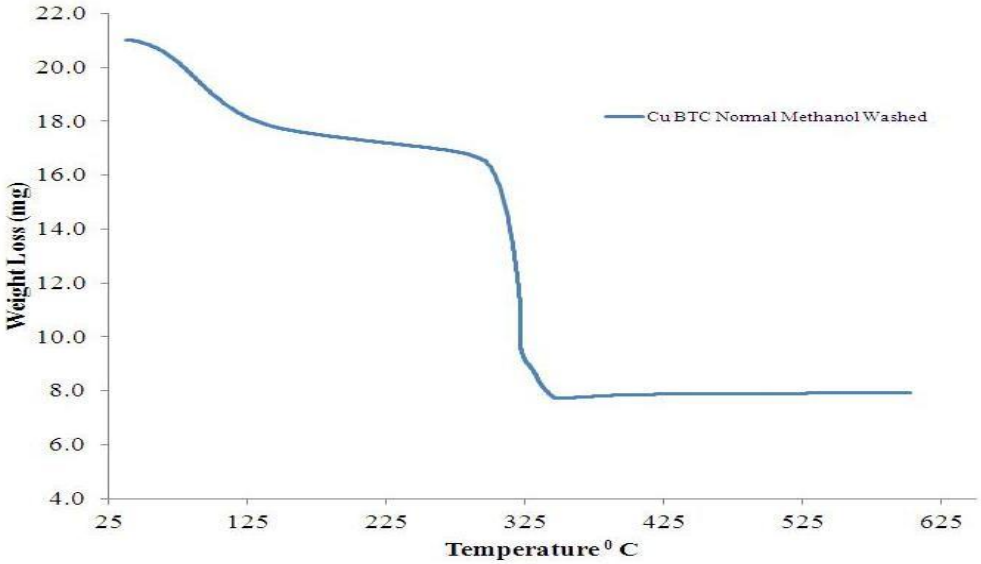

Figure 4.4: TGA Analysis of as-synthesized Cu-BTC Sample

4.1.2 Characterization of Activated Carbon

4.1.2.1 SEM Analysis

The SEM image is shown in the following figure. The surface morphology of commercial activated carbon used specifically for this work matches well with various types of activated carbons reported in the literature.

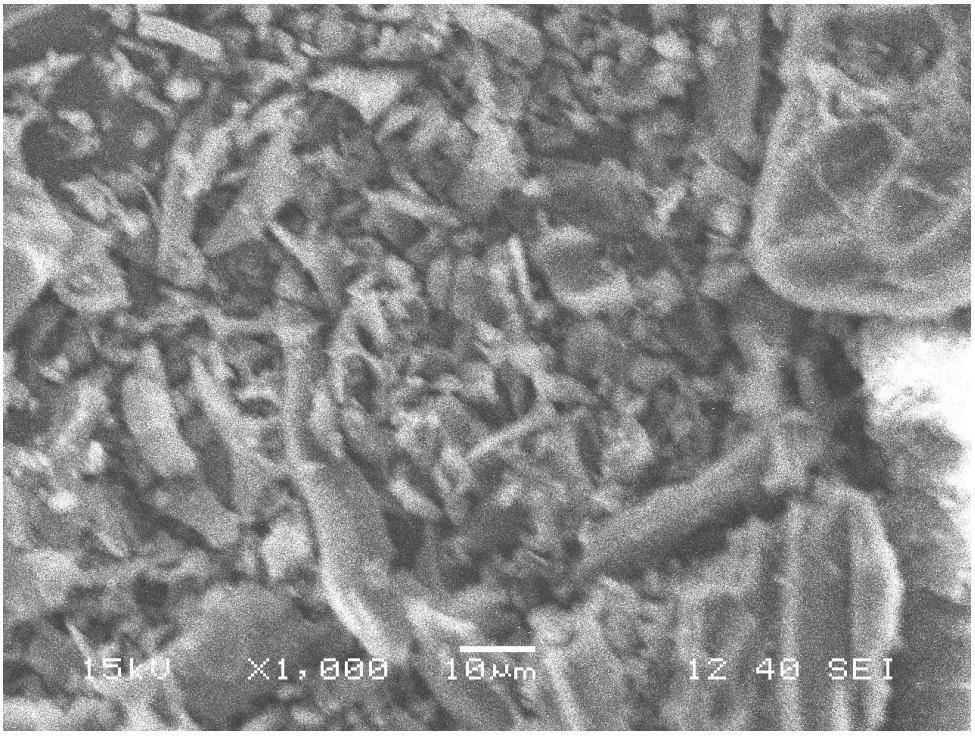

Figure 4.5: SEM Image of Commercial Grade Activated Carbon (Merck)

4.1.2.2 TGA Analysis

The TGA profile of the activated carbon is shown in figure 4.6. The thermal stability of activated carbon is much higher than Cu-BTC and hence more effective in high temperature applications.

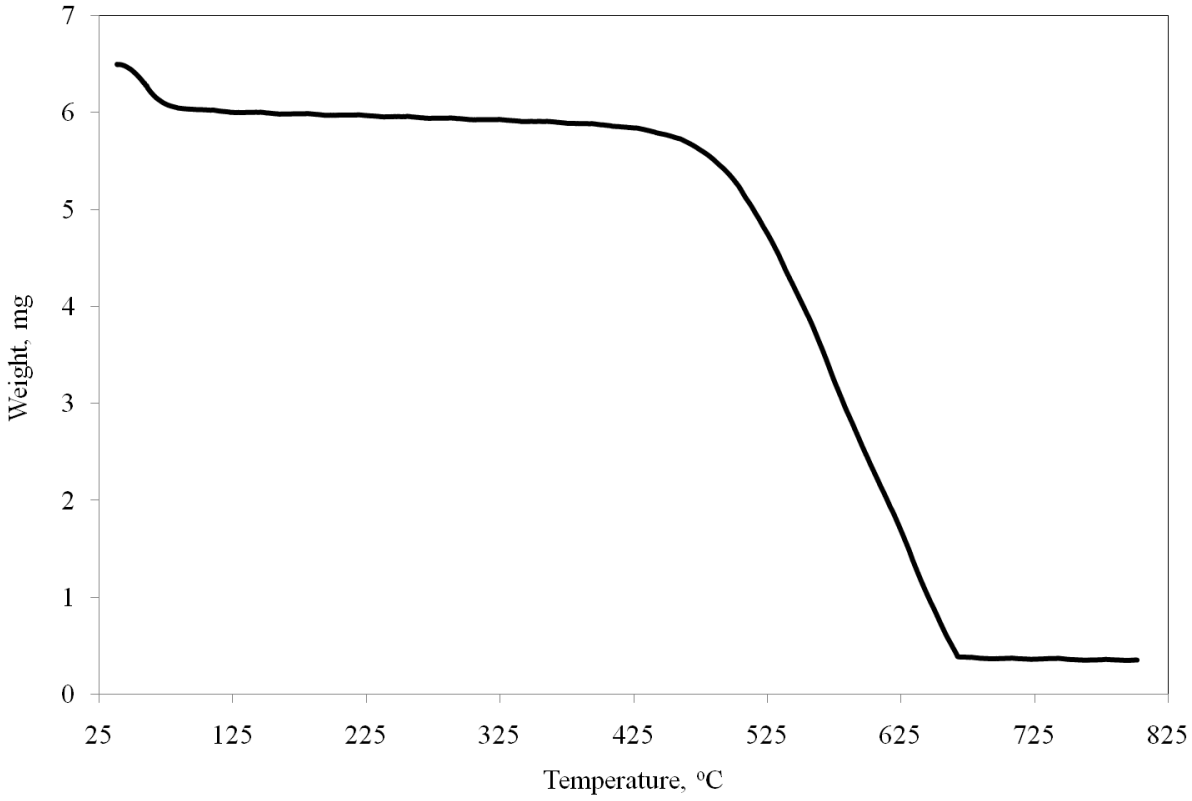

Figure 4.6: TGA profile of activated carbon (Merck)

4.1.2.3 Powder XRD Analysis

Powder X-ray diffraction analysis is shown in figure 4.7. It establishes the amorphous nature of activated carbon.

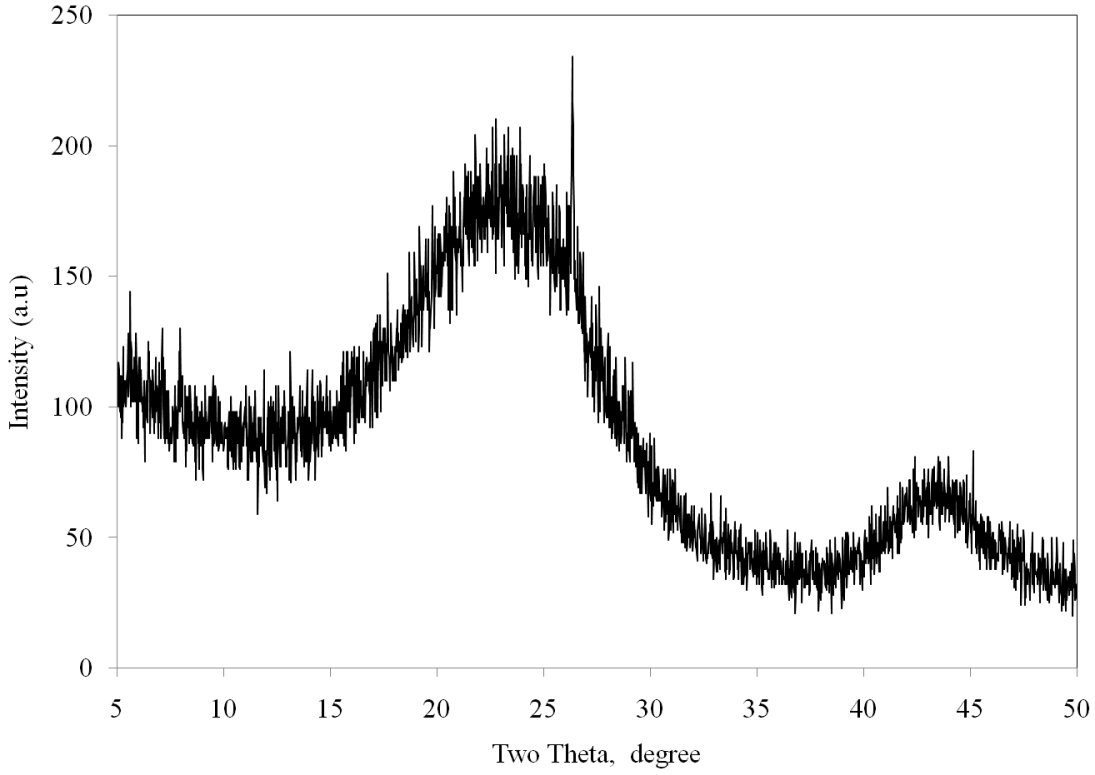

Figure 4.7: Powder XRD pattern of activated carbon (Merck)

4.2 DYE REMOVAL STUDY WITH Cu-BTC

4.2.1 Effect of adsorbent dose

As is evidenced from the above plot, the results on removal of Rhodamine B from an aqueous medium do not yield an encouraging result with Cu-BTC. A detailed data sheet is included in the ***appendix***. This came as a surprise to our expectation since Cu-BTC possess all the necessary properties to be effectively removing Rhodamine B. Not only the removal percentage was meager but also it appeared that the Cu-BTC tend to lose sheen and disintegrate in aqueous medium on prolonged exposure, necessitating a comprehensive study on the stability of Cu-BTC in aqueous medium under various circumstances.

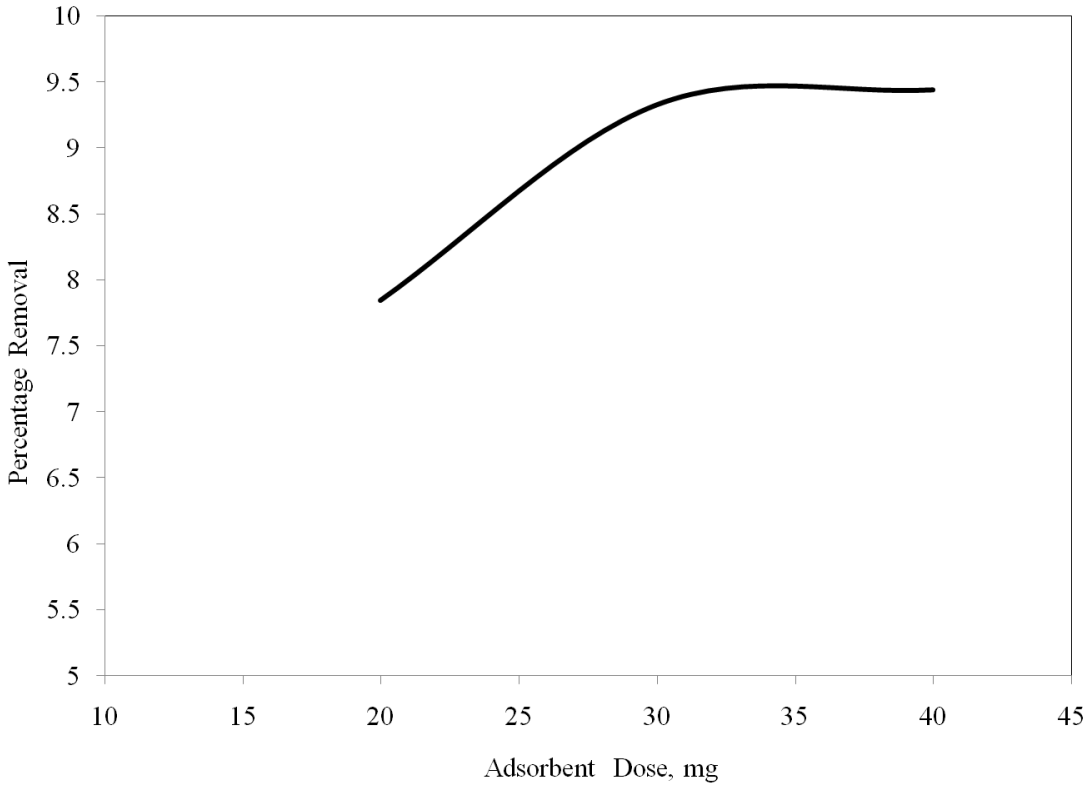

Figure 4.8: Effect of adsorbent dose i.e. Cu-BTC on removal of Rhodamine B

4.2.2 Stability Analysis of Cu-BTC in Aqueous Medium

Stability analysis of Cu-BTC was carried out at ambient conditions under solution pH varying from 1 to 12, meaning extremely acidic medium to high alkaline medium. To maintain a standard pH value for each batch, a buffer was used. The details about buffers are given in ***appendix 3***.

A standard amount of Cu-BTC was weighed and added equally to each beaker containing de-ionized water (with buffer solution mixed with it). The beakers were corked properly and placed in a water bath shaker maintained at 30^{o}C for 120 minutes. We made sure that the mixing was

adequate. The solution from the each of the beaker was then transferred to centrifuge vials and an rpm of 4000 was set for 10 minutes to precipitate all of Cu-BTC. After separating Cu-BTC from the solution, it was washed with DMF (to remove the dissociated BTC) and methanol respectively to get back to its previous properties. Figure 4.9 shows the results for all the batches.

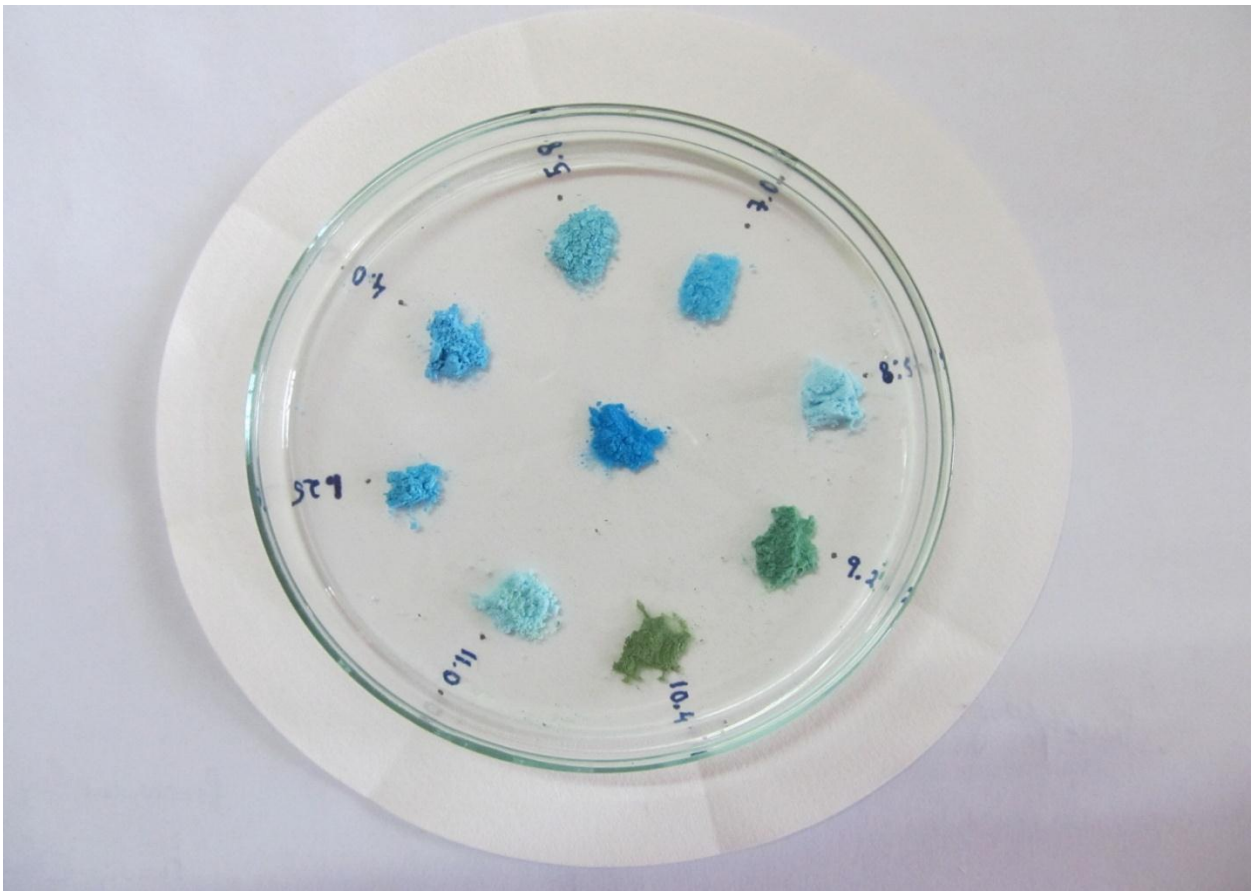

Figure 4.9: Stability analysis of Cu-BTC in aqueous medium at various pH conditions

The original Cu-BTC sample (post synthesis) is shown at the centre of the petridish whereas products treated under various pH conditions are shown along the rim. This digital camera image (Sony cybershot, W-35) quite clearly shows that the variation of pH and long exposure in aqueous medium have a detrimental effect on the structural stability of Cu-BTC. Although, in and around a neutral pH regime of 7.0, the effect is minimal but as we move along highly acidic

or alkaline medium, the effect is drastic and there is a complete metamorphosis of Cu-BTC especially in cases between pH: 9-11.

The physical observation with naked eyes itself a clear indication of structural deformity but the packing density measurements also corroborate the findings. Generally, a standard Cu-BTC sample has a bulk packing density of approximately 0.5-0.6 gm/cc. But here due to structural collapse the packing density of different batches of Cu-BTC have significantly reduced.

4.2.3 SEM Analysis of Cu-BTC Sample [Post Exposure to Aqueous Medium]

Figure 4.10 shows the image of one of the batch of Cu-BTC after prolonged exposure in aqueous medium. It is very clear from the image that the crystalline morphology of Cu-BTC severely hampered on long contact with water.

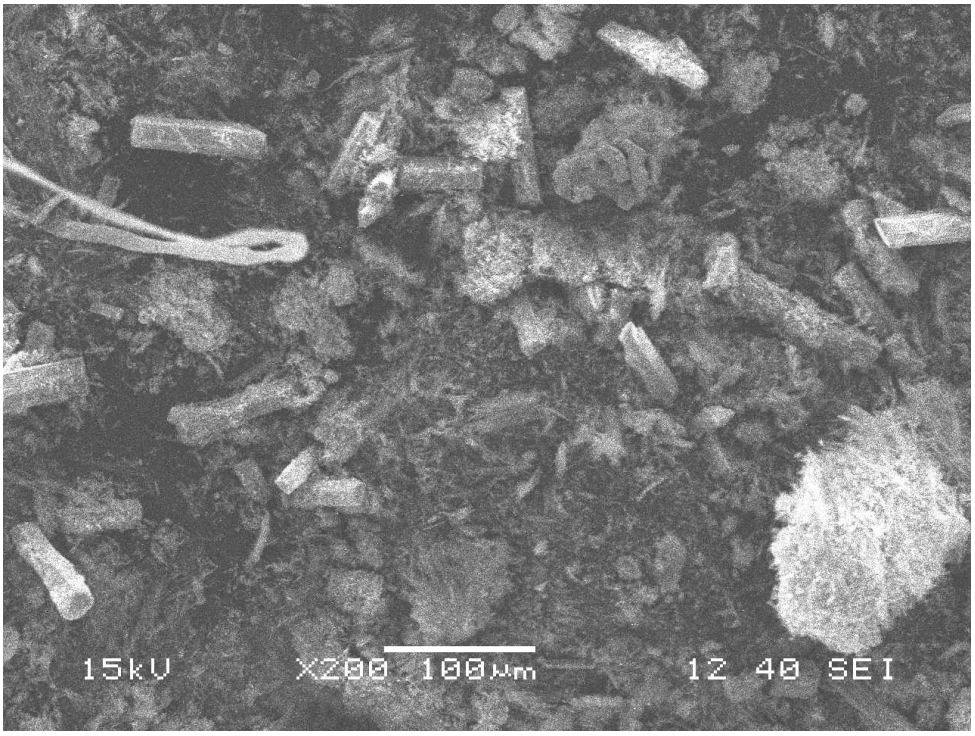

Figure 4.10: SEM image of Cu-BTC after treatment with Rhodamine B

4.2.4 Powder XRD Analysis of Cu-BTC Sample [Post Exposure to Aqueous Medium]

Figure 4.11 shows the powder X-ray diffraction pattern post exposure to aqueous medium. It is amply clear that the crystalline nature of Cu-BTC is slowly disappearing on long exposure to aqueous medium.

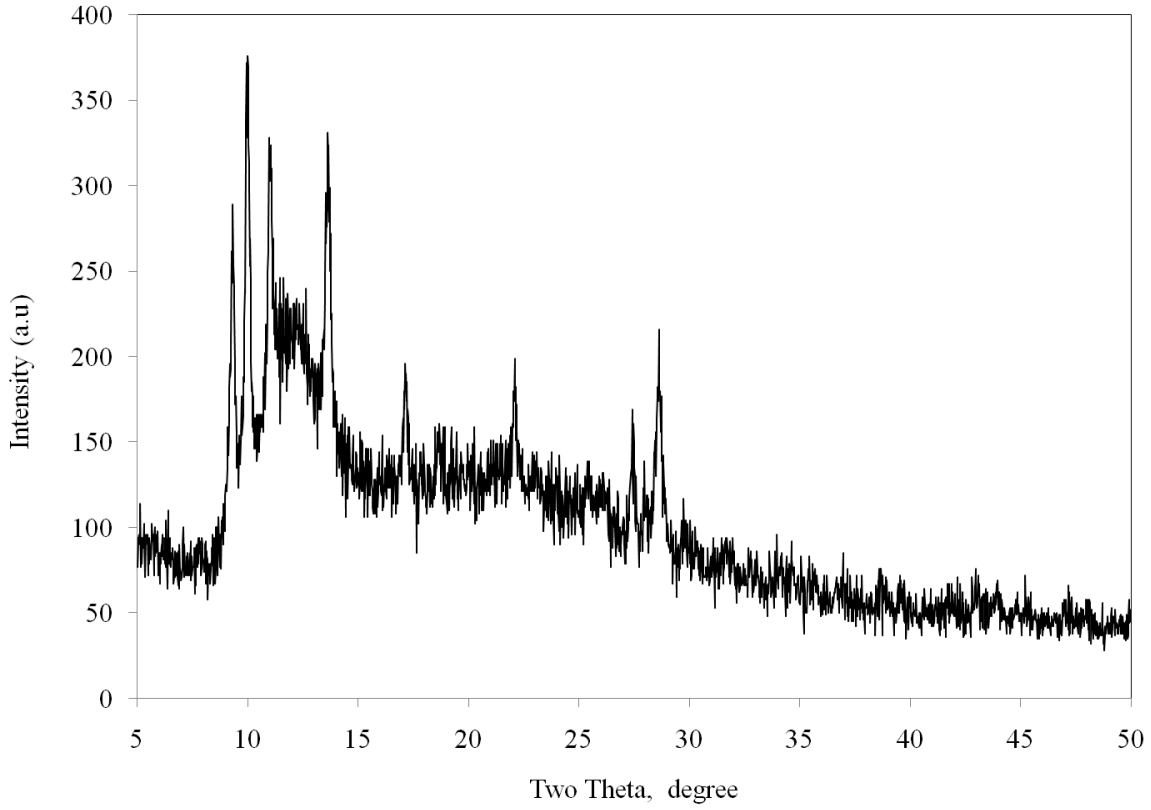

Figure 4.11: Powder XRD profile of Cu-BTC after treatment with Rhodamine B

4.2.5 TGA Analysis of Cu-BTC Sample [Post Exposure to Aqueous Medium]

Figure 4.12 shows the TGA analysis of Cu-BTC sample after being exposed to aqueous medium for a long time. Although final degradation temperature (275^{o}C) remains same but the uneven nature of the curve is an indication of structural deformation.

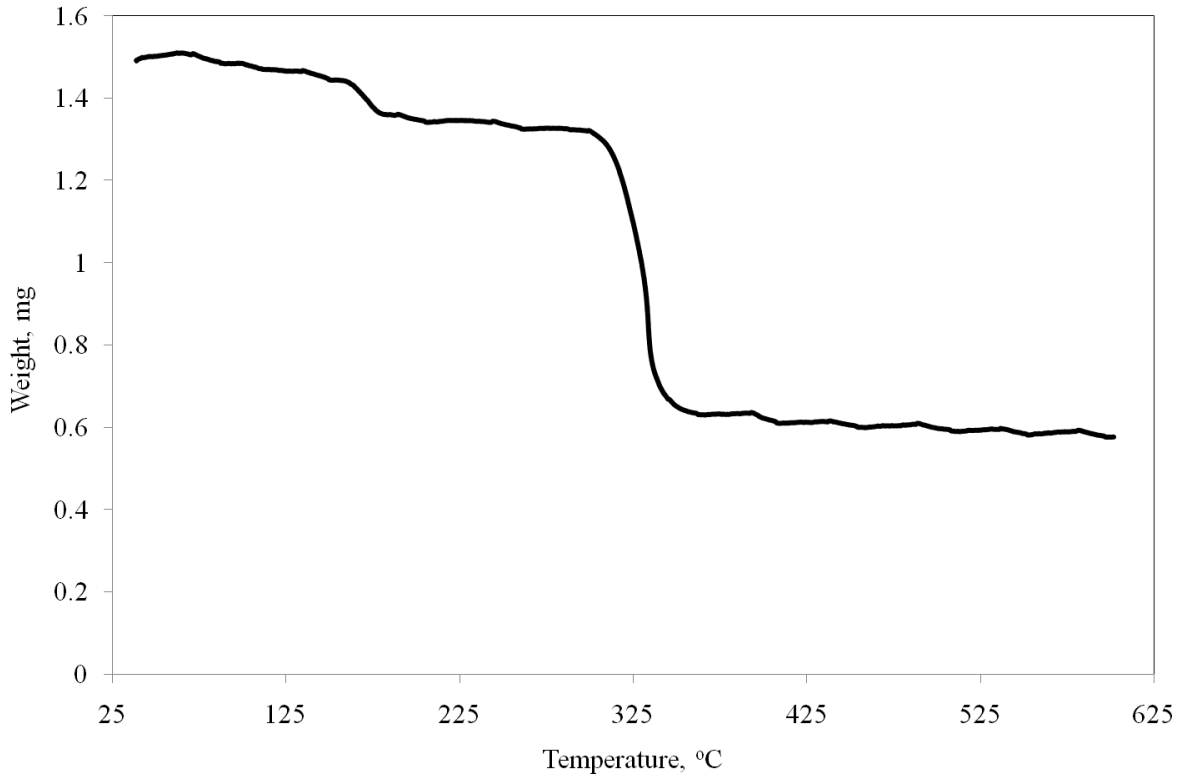

Figure 4.12: TGA profile of Cu-BTC [Post Exposure to aqueous Medium]

4.3 DYE REMOVAL STUDY WITH ACTIVATED CARBON

4.3.1 STUDY ON RHODAMINE B

In the following paragraphs the complete study is analyzed.

4.3.1.1 Effect of adsorbent dose

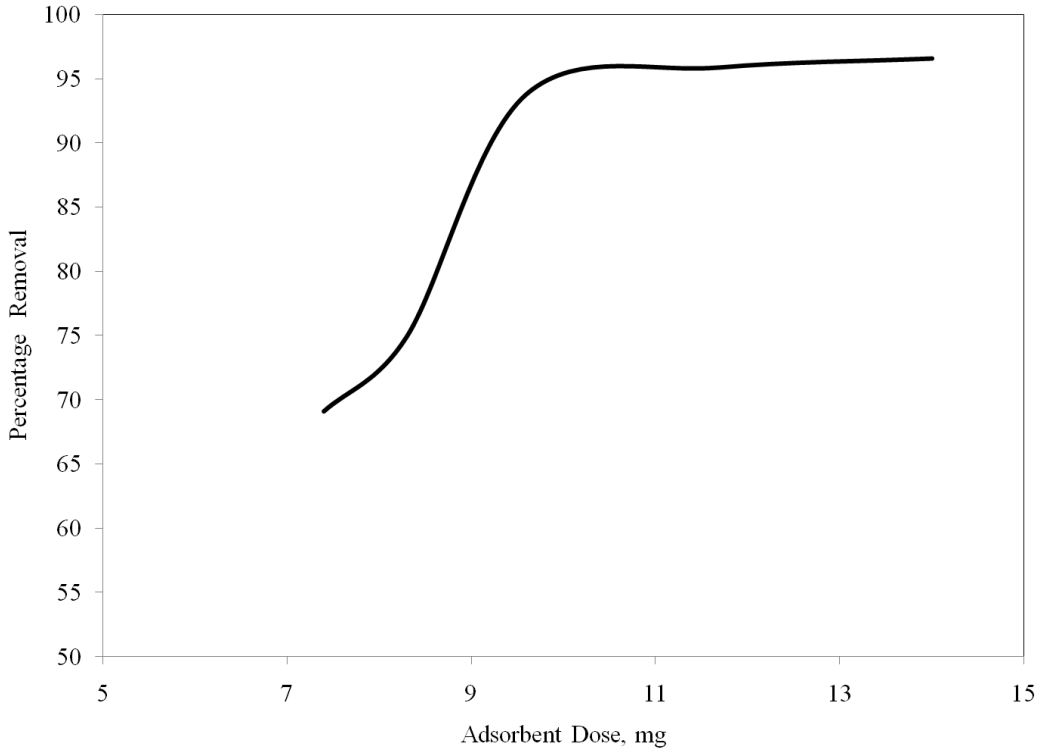

Figure 4.13: Effect of Adsorbent dose (Rhodamine B on Commercial Activated Carbon)

The values of percentage removal with varying adsorbent dose for this case are given in ***appendix 4***.

From the figure above, we can infer that the optimum adsorbent dose is 10 mg/50 ml solution. Though, there is an increase in % removal of Rhodamine B on further addition of adsorbent but this increase is marginal and from an economic point of view, it might not be a wise step to use adsorbent more than 10 mg/ 50 ml solution.

4.3.1.2 Effect of initial pH

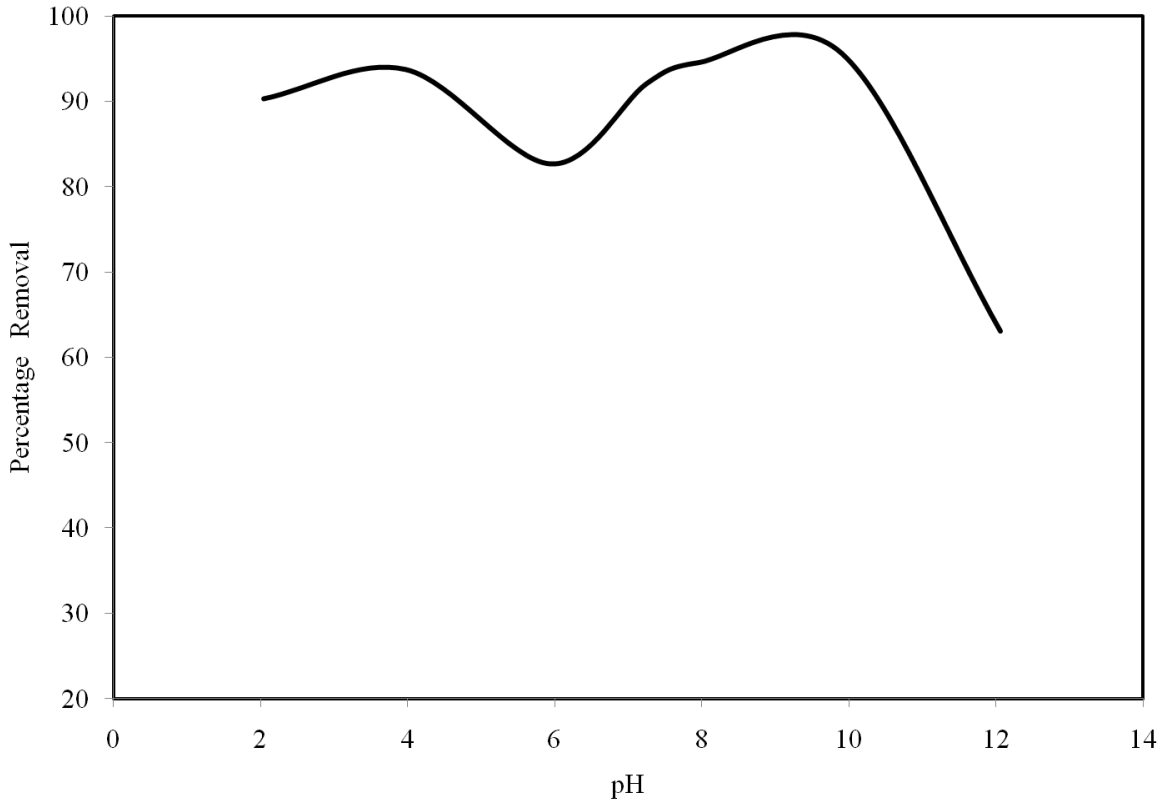

Figure 4.14: Effect of initial pH (Rhodamine B on Commercial Activated Carbon)

The values of percentage removal for different initial pH are given in ***appendix 4***.

The adsorption of dye on the surface of activated carbon can be explained basically on two types of interactions.

- Physisorption based on van der walls interaction due to hydrogen bonding.
- Electrostatic interaction due to polarized functional groups on the surface of the adsorbent due to solvent interaction.

For electrostatic interaction to occur the charge on the surface being the important factor depends on the nature of the solvent. It is to be noted that that the dye is basic in nature. From the literature it can be noted the surface of activated carbon is amphoteric in nature due to which alteration in pH causes polarization of surface in varying degree. Hence, for chemisorption to occur the charge on the activated carbon should carry negative charge. From the figure above, it can be seen that high basic environment (say pH 12) shows least adsorption (i.e. around 63% removal). Hence, the removal of the dye can be due to hydrogen bonding and van der wall interaction between the dye and the surface on the adsorbent.

For lower pH condition (around pH= 4) and higher pH condition (around 10), the removal of the dye is more favorable due to the presence of carbonyl and hydroxyl functional groups on the surface on the adsorbent. In acidic condition, the functional groups on the adsorbent surface polarize thereby creating electrostatic interaction along side with hydrogen bonding and van der walls interaction.

Within neutral pH range of (6-7) drop in adsorption (percentage removal about 83 %) could be due to drop in polarization of surface of activated carbon.

Though, the above observations are subjected to more experimentations.

4.3.1.3 Effect of Contact Time

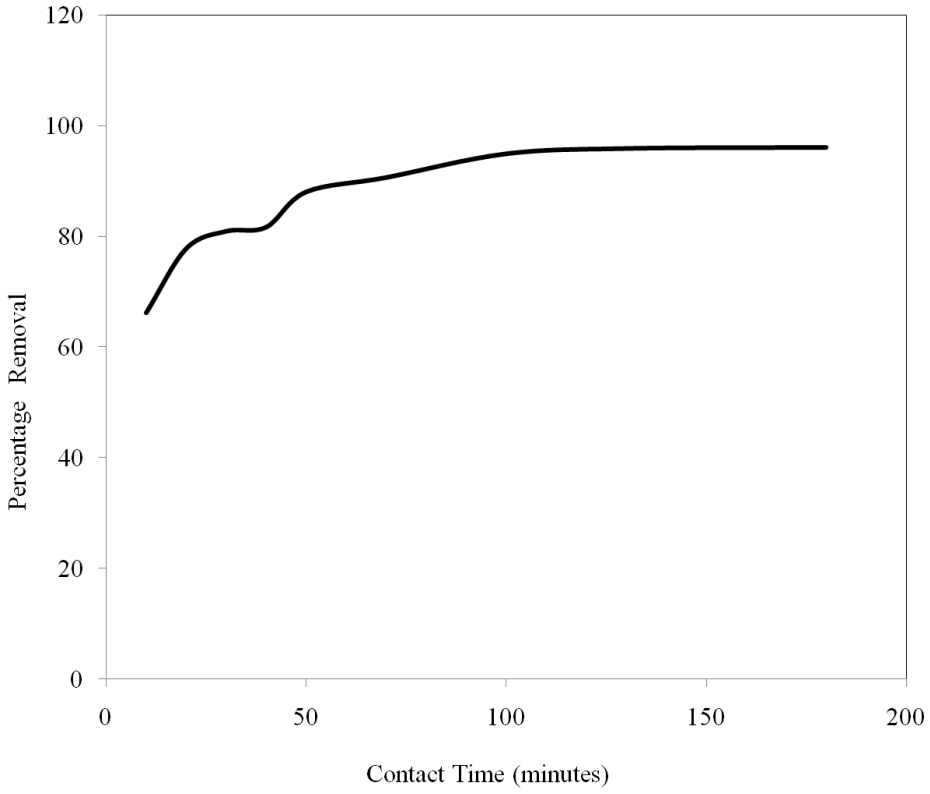

Figure 4.15: Effect of contact time (Rhodamine B on Commercial Activated Carbon)

The values of percentage removal for different time intervals are shown in ***appendix 4***.

As can be seen from the figure above that adsorption increases more rapidly at the initial time period and rate of adsorption decreases as we proceed to the saturation limit. The equilibrium can be assumed to have achieved after 100 minutes as, the final dye concentration does not seem to increase much after this limit. The reason might be the saturation of the active sites which do not allow further adsorption to take place.

4.3.2 STUDY ON ERIOGLAUCINE

4.3.2.1 Effect of Adsorbent Dose

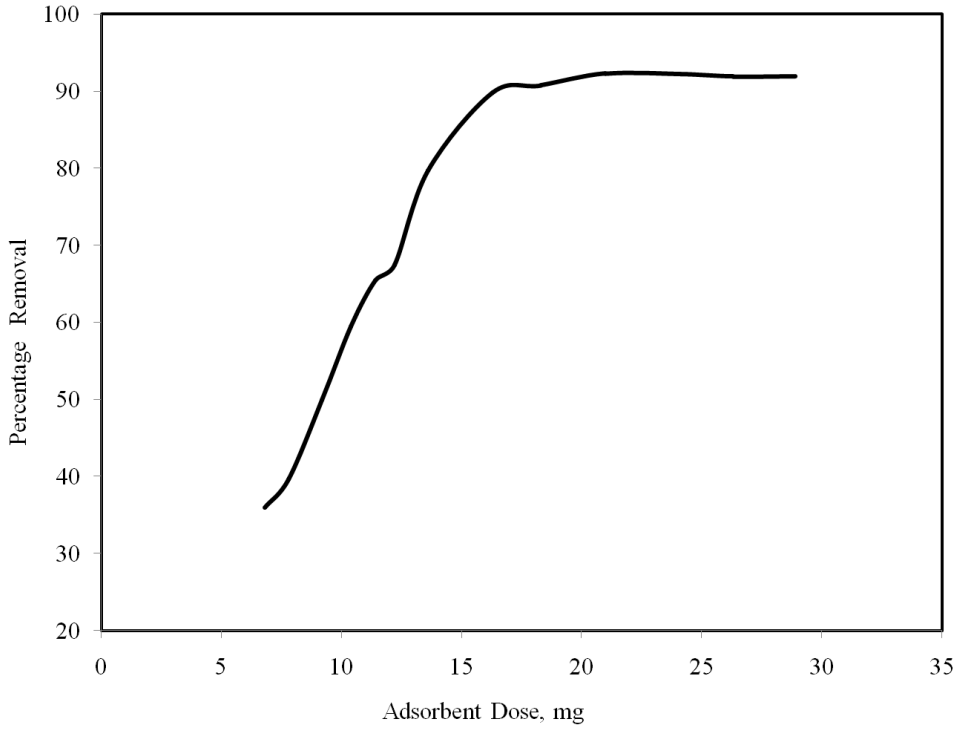

Figure 4.16: Effect of adsorbent dose (Erioglaucine on Commercial Activated Carbon)

The values of percentage removal with varying adsorbent dose are given in ***appendix 5***.

From the figure above, it is concluded that adsorbent dose for the most economical use is 20 mg/50 ml solution, as beyond this dose, there is not much increase in the adsorption.

4.3.2.2 Effect of initial pH

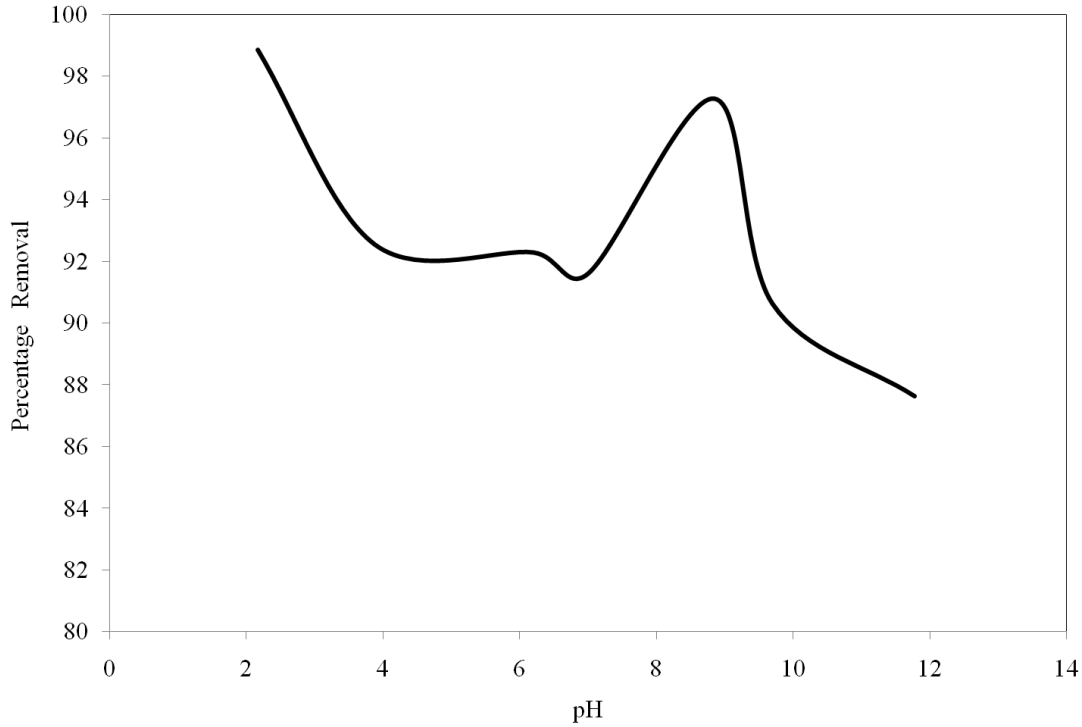

Figure 4.17: Effect of initial pH (Erioglaucine on Commercial Activated Carbon)

The values of percentage removal with different initial pH are given in ***appendix 5***.

The figure above can also be explained based on the observations of the effect of initial pH of Rhodamine B on activated carbon. For lower pH condition (around pH= 2) and higher pH condition (around 9), the removal of the dye is more favorable due to the presence of carbonyl and hydroxyl functional groups on the surface on the adsorbent. In acidic condition, the functional groups on the adsorbent surface polarize thereby creating electrostatic interaction along side with hydrogen bonding and van der walls interaction.

Here, also the observations are based on further experimentations.

4.3.2.3 Effect of Contact Time

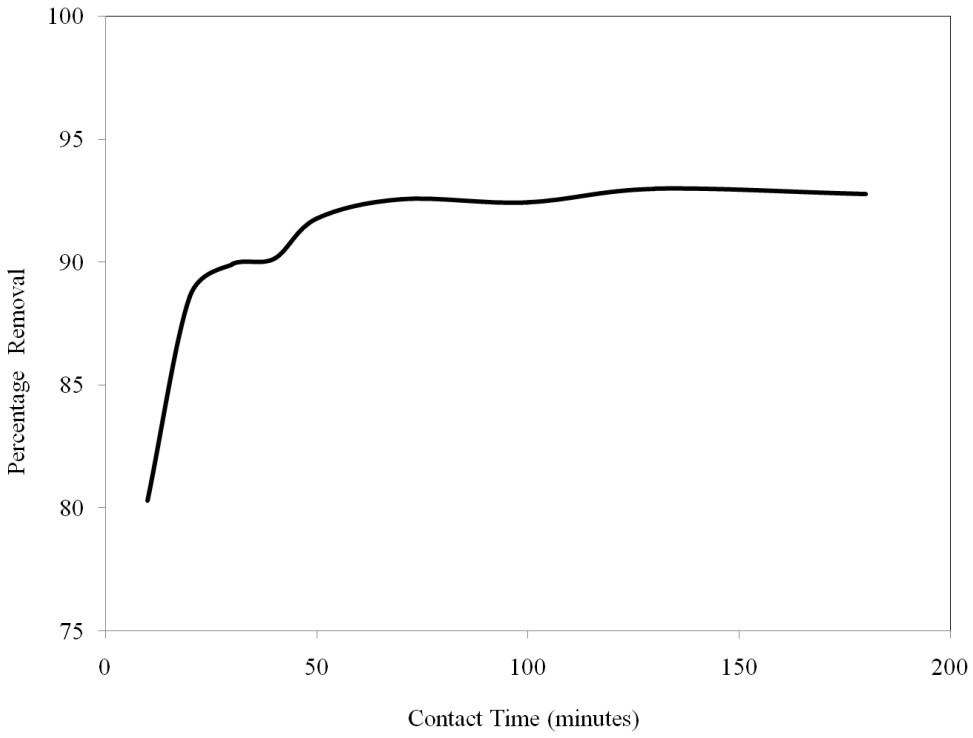

Figure 4.18: Effect of Contact Time (Erioglaucine on Commercial Activated Carbon

The values of percentage removal for different time intervals are given in ***appendix 5***.

From the figure above, it can be estimated that the equilibrium is reached after 70 minutes, as there is not much increase in the percentage removal after this time period.

CHAPTER 5

CONCLUSIONS AND FUTURE WORKS

5.1 Conclusions

Despite the fact that Metal Organic Frameworks have (MOFs) attracted the attention of vivid researches across the globe due to their large surface area, high tunability and various applications, but still there lies some concerns over using these types of structures for liquid phase adsorption. Our observations do not envisage Cu-BTC, a kind of MOF, as an effective adsorbent for prolonged exposure in aqueous medium.

On the other hand, Commercial Activated Carbon showed some encouraging results in the study of adsorption for both the dyes (Rhodamine B and Erioglaucine). The optimum conditions of adsorption (adsorbent dose, initial pH, contact time) for both the dyes on Commercial Activated Carbon were also estimated.

5.2 Future Works

The observations in this paper are subjected to further experimentations. Some of the parameters to study can be:

- BET Analysis of Cu-BTC sample (Post treatment to adsorption)
- Adsorption isotherms
- Kinetic models

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APPENDICES

APPENDIX 1

Preparation of solutions to study the effects of Cu-BTC

Preparation of 200 ml of stock solution (10^{-4} M)

Type of dye	**Amount of dye used (mg)**	**RO water used (ml)**
Rhodamine B	9.58	200 ml
Erioglaucine	15.8	200 ml

Preparation of 50 ml of working solution (10^{-5} M)

Stock solution (10^{-4} M) used (ml)	**RO water used (ml)**
5	45

APPENDIX 2

Preparation of solutions to study the effects of Activated Carbon

Preparation of 100 ml of stock solution (1000 mg/l)

Amount of dye used (mg)	**RO water used (ml)**
100	100

Preparation of 50 ml of working solution (20 mg/l)

Amount of stock solution (10^{-4} M) used (ml)	**RO water used (ml)**
1	49

APPENDIX 3

Study of Cu-BTC on Removal of Rhodamine B

Effect of adsorbent dose

Adsorbent dose (mg)	**Percentage removal (%)**
20	7.8470
30	9.4429
40	9.3296

Buffer solutions used

pH	**Buffer**
1.25	KCl + HCl
4	Standard pellet
5.8	Acetate
7	Standard
8.5	Bicarbonate
9	Standard
11	Bicarbonate + NaOH

APPENDIX 4

Study of Activated Carbon on Removal of Rhodamine B

Effect of adsorbent dose

Adsorbent dose (mg)	**Percentage removal (%)**
7.4	69.1071
8.3	74.9253
9.6	93.7952
11.7	95.8621
14.0	96.5569

Effect of initial pH

Initial pH	**Percentage removal (%)**
2.04	90.3037
3.97	93.7342
5.94	82.6796
7.25	92.0910
7.95	94.5276
9.9	95.6361
12.06	63.1032

Effect of contact time

Contact time (minutes)	**Percentage removal (%)**
10	66.1413
20	77.7357
30	80.8618
40	81.5992
50	87.9641
70	90.5661
100	94.8492
130	94.8004
180	96.0012

APPENDIX 5

Study of Activated Carbon on Removal of Erioglaucine

Effect of adsorbent dose

Adsorbent dose (mg)	**Percentage removal (%)**
6.8	35.9937
7.8	39.6708
9.2	49.9612
10.4	59.5199
11.4	65.4655
12.2	67.4964
13.6	79.6893
16.3	89.8186
18.3	90.7441
21.0	92.3034
24.1	92.2576
26.3	91.8839
28.9	91.9352

Effect of initial pH

Initial pH	**Percentage removal (%)**
2.16	98.8578
3.88	92.5272
6.20	92.2798
7.00	91.6006
8.85	97.2753
9.70	90.6097
11.78	87.6142

Effect of contact time

Contact time (minutes)	**Percentage removal (%)**
10	80.3090
20	88.6090
30	89.9087
40	90.1315
50	91.7564
70	92.5461
100	92.4261
130	92.9823
180	92.7524